been calculated neglecting the value obtained for the highest nitrite ion concentration. It can be seen that the agreement between the $k_1^{NO_2^-}$ and $k_1^{Cl^-}$ is extraordinarily good. If the neglected value at highest [NO_2^-] were also used, then the average k_1 becomes 5.05×10^{-5}, which is still a very satisfactory value.

<div align="center">

TABLE IV

RATES CONSTANTS FOR THE REACTION OF trans-[Pt(PEt$_3$)$_2$Cl$_2$] WITH ^{36}Cl$^-$ AND NO$_2^-$ IN CH$_3$OH AT 55°

</div>

Reactant	k_1, sec.$^{-1} \times 10^5$	k_2, M^{-1} sec.$^{-1} \times 10^4$
^{36}Cl$^-$	4.5	4.20
NO$_2^-$	4.47	0.97

The kinetic data for several Pt(II) complexes in water indicate that the effectiveness of NO$_2^-$ as a reagent, as compared to Cl$^-$, is much greater for the neutral and anionic complexes, e.g., [Pt(NH$_3$)$_2$Cl$_2$] and [PtCl$_4$]$^{2-}$, than for cationic complexes. Indeed, for [Pt(dien)H$_2$O]$^{2+}$ the reactivity order is inverted. A comparison of k_2 values between the substitution and chlorine exchange reactions is given in Table IV. The ratio $k_2^{NO_2^-}/k_2^{Cl^-}$ is of the order of magnitude found for positively charged complexes in water.[13]

That NO$_2^-$ can act as an electrophilic agent can easily be understood if one considers that it has an empty antibonding π-orbital where charge can be transferred from the metal atom. If 14 of the 18 outer shell electrons of the nitrite ion are put in its bonding orbitals and lone pair orbitals, there are 4 electrons left for occupation of three π-orbitals. These are orbitals arising from the combination (p$_{z_1}$ + p$_{z_2}$) + λp$_{zN}$ (bonding, filled), p$_{z1}$ − p$_{z2}$ (nonbonding, filled), and λ(p$_{z1}$ + p$_{z2}$) − p$_{zN}$ (antibonding, empty), written in order of increasing energy. The antibonding orbital is probably of too high an energy to combine with the π-platinum orbitals. However, the drift of electrons in the N → Pt σ-bond will cause the energy of the antibonding or-
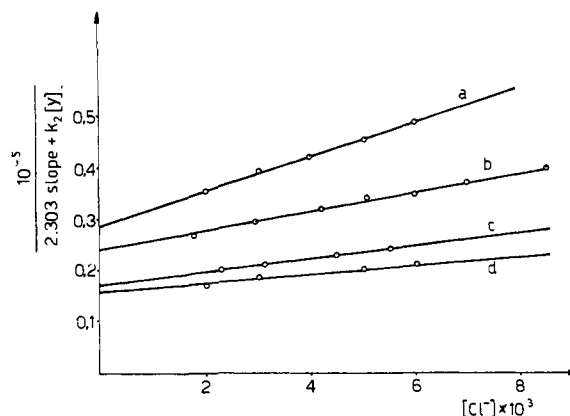

Fig. 4.—Graphical derivation of k_1 using stationary state treatment (Y = NO$_2^-$): a, [Y] = 0.1; b, [Y] = 0.15; c, [Y] = 0.2; d, [Y] = 0.25.

bital to be lowered, becoming thus accessible for bond formation with platinum. This empty orbital must be more localized on the less electronegative nitrogen atom. In this way the electrophilic nature of the nitrite ion may arise from a sort of synergic O$_2$N $\overset{\sigma}{\underset{\pi}{\rightleftarrows}}$ Pt interaction. However, when the platinum atom is bonded to strong π-electron acceptor ligands, the energy of its π-electrons will be lowered and the π-attack of the nitrite ion will become less favorable.

The results presented here are consistent with the assumption made that π-bonding may be of importance in determining the effectiveness of NO$_2^-$ as an electrophilic reagent.

Anation of the trans-Aquonitrobis-(ethylenediamine)-cobalt(III) Ion in a Tetramethylene Sulfone–Water Mixture[1]

BY C. H. LANGFORD AND M. P. JOHNSON

The rates of entry of the anions Cl$^-$, Br$^-$, NO$_3^-$, and SCN$^-$ into trans-[Co(en)$_2$NO$_2$OH$_2$]$^{++}$ (en = ethylenediamine) were found to differ by no more than a factor of four in the solvent 7.8% aqueous tetramethylene sulfone. The reactions were nearly zero order in the anion concentration. Conductance data on a model system strongly suggest that the observed reactions take place within outer-sphere complexes. The insensitivity of the rate to changes in the nature of the entering group suggests no more than weak bonding of the entering group to cobalt in the transition state.

Introduction

Hydrolysis reactions of Co(III) amine complexes have been the subject of intensive study,[2] but the reverse reaction, "anation," has received much less attention. Yet anation has not only its intrinsic in-

terest but also offers information about the transition state of the hydrolysis process through application of the principle of microscopic reversibility.

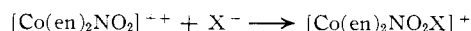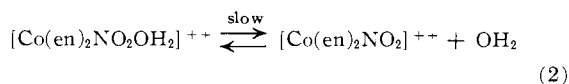The kinetics of reaction 1 in aqueous solution using the cis isomer were investigated by Basolo, Stone,

$$[Co(en)_2NO_2OH_2]^{++} + X^- \longrightarrow [Co(en)_2NO_2X]^+ + H_2O \quad (1)$$
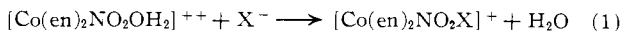
Bergmann, and Pearson.[3] They found that the reaction was first order in the complex, first order in the

(1) From a thesis by M. P. J. submitted in fulfillment of a requirement for the B.A. degree with honors, Amherst College, 1963. This work was supported by a grant from the Research Corporation and presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 8–13, 1963.
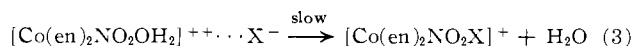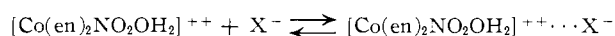
(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(3) F. Basolo, B. D. Stone, J. G. Bergmann, and R. G. Pearson, J. Am. Chem. Soc., **76**, 3079 (1954).

entering ion, and second order over-all throughout a wide range of anion concentration. Unfortunately, this result is consistent with more than one reasonable mechanism. At least three separate formulations have been discussed. The most obvious is the simple S_N2 reaction for which no more than eq. 1 need be written. As Basolo, et al., noted, a scheme with an S_N1 slow step is also consistent with the kinetic result. This is shown in (2). In (2), it is assumed that loss of water

$$[Co(en)_2NO_2OH_2]^{++} \overset{slow}{\rightleftharpoons} [Co(en)_2NO_2]^{++} + OH_2$$

$$[Co(en)_2NO_2]^{++} + X^- \longrightarrow [Co(en)_2NO_2X]^+ \qquad (2)$$

and formation of the five-coordinate intermediate is the slow step but that there may be competition for the intermediate between water and X^- leading to $[X^-]$ dependent kinetics. The third interpretation of these kinetics follows the suggestion of Taube and co-workers[4,5] that the anation reaction takes place by interchange of ligands between the outer and inner coordinations spheres (i.e., within an ion pair). For this version we could write scheme 3. The transition

$$[Co(en)_2NO_2OH_2]^{++} + X^- \rightleftharpoons [Co(en)_2NO_2OH_2]^{++}\cdots X^-$$

$$[Co(en)_2NO_2OH_2]^{++}\cdots X^- \overset{slow}{\longrightarrow} [Co(en)_2NO_2X]^+ + H_2O \qquad (3)$$

state of the slow step in outer sphere–inner sphere interchange is not illuminated at all by knowledge of the rate law.

A kinetic analysis of schemes 2 and 3 indicates that interesting data ought to emerge from experiments at high entering anion activity and/or low water activity. In terms of (2), these conditions could lead to X^- overwhelming water in the competition for the intermediate and a limiting case of first-order kinetics. In terms of (3) these conditions could lead to 100% ion pairing and a limiting case of first-order kinetics. This report describes the kinetics of reaction 1 using the *trans* isomer in a solvent mixture of tetramethylene sulfone and water (7.8% by vol. water) where the limiting conditions might be expected to be fulfilled.

Experimental

Materials.—*trans*-[Co(en)_2NO_2Cl]NO_3 was prepared from *trans*-[Co(en)_2(NO_2)_2]NO_3 by Werner's method[6] and converted to the perchlorate by precipitation with perchloric acid. *trans*-[Co(en)_2NO_2OH_2](ClO_4)_2 was obtained in aqueous solution by treating the chloro complex with the required amount of AgClO_4. Its identity was checked spectrophotometrically. *trans*-[Co(en)_2-NO_2NH_3]ClClO_4 was obtained by dissolving *trans*-[Co(en)_2NO_2Cl]-ClO_4 in liquid ammonia and allowing the ammonia to evaporate slowly. *Anal.* Calcd. for CoC_4H_19N_2O_6Cl_2: C, 12.73; N, 22.25. Found: C, 12.78; N, 22.48. The perchlorate salt was obtained by treating an aqueous solution of the chloride perchlorate with AgClO_4. The chloride salt was obtained by treating an aqueous solution of the chloride perchlorate with the required amount of tetraphenylarsonium chloride.

Anions of interest were introduced as tetraphenylarsonium salts for maximum solubility. Reagent grade tetraphenylarsonium chloride was obtained from G. F. Smith Chemical Co. Tetraphenylarsonium bromide was prepared by converting the chloride to the hydroxide with Ag_2O and precipitating with concentrated aqueous HBr. Tetraphenylarsonium thiocyanate was obtained analogously except that the acid was obtained by passing aqueous KCNS through an Amberlite IR-120 ion-exchange column in the acid form. The perchlorate and nitrate salts precipitate directly when an aqueous solution of the chloride is treated with the concentrated acid. The salts may be recrystallized from water.

(4) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953).

(5) W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963).

(6) A. Werner, *Ann.*, **386**, 1 (1912).

Tetramethylene sulfone was obtained from the Phillips Petroleum Co. and distilled at 1–2 mm. from powdered NaOH. Distilled water was deionized prior to use.

Kinetic Measurements.—Anation rates were determined spectrophotometrically using a Beckman DU spectrophotometer with the cell chamber thermostated at 30.0 ± 0.1°. In all experiments, the procedure was to thermostat 3.00 ml. of a sulfone solution of the tetraphenylarsonium salt in the cell and then to add 0.250 ml. of the aqueous solution of *trans*-[Co(en)_2NO_2OH_2]^{++}. The final complex concentration was in the range 2 to 3 × 10^{-3} M. The anion concentrations were varied from 1.6 × 10^{-3} to 0.12 M. All reactions were followed for at least three half-life periods. The wave lengths chosen were: Cl^-, 520 mμ; Br^-, 520 mμ; NO_3^-, 480 mμ; SCN^-, 465 mμ. Rate constants were obtained from the usual first-order plots. Product identity was verified by recording complete "infinity time" spectra on a Bausch and Lomb Spectronic 505 recording spectrophotometer. The rate constants were reproducible to ±5%. This relatively low precision results from the combined circumstances of small absorbance changes and fast reactions.

Conductance Measurements.—Conductance measurements on the model compounds *trans*-[Co(en)_2NO_2NH_3]Cl_2 and *trans*-[Co(en)_2NO_2NH_3](ClO_4)_2 in the sulfone-water solvent were made at 30.0° using a conventional, simple Wheatstone bridge and a cell with bright Pt electrodes (cell constant = 0.3). The concentration range surveyed was 1 × 10^{-5} to 6 × 10^{-3} M.

Results

Our first experiments on reaction 1 in the sulfone solvent surveyed the rates of entry of all anions with concentration ratios chosen to produce pseudo-first-order kinetics. The complex concentration was either 2.0 × 10^{-3} or 3.0 × 10^{-3} M and the anion concentration was varied from 0.01 to 0.12 M. The reactions were first order in the complex concentration and showed no significant dependence on anion concentration. The first-order rate constants are collected in Table I. With the exception of thiocyanate, the nature of the anion seems unimportant; thiocyanate entry is about one half as fast as the other reactions. The variation in aquo complex concentration had no effect.

TABLE I

FIRST-ORDER RATE CONSTANTS AT 30° FOR ANATION OF *trans*-[Co(en)_2NO_2OH_2]^{++} BY VARIOUS ANIONS IN A TETRAMETHYLENE SULFONE-WATER MIXTURE (7.8% H_2O)

Rate constants are given in sec.$^{-1}$ × 10^2 under the heading of the anion

Anion concn., M	Cl^-	Br^-	NO_3^-	SCN^-
0.010	1.5			0.41
.020	1.2			
.033	1.4	1.4	1.3	0.51
.060	1.3	1.4	1.1	.52
.080	1.3	1.6	1.1	.50
.120	1.1	1.4	1.2	.52

Reactions of the aquo complex with chloride and thiocyanate were studied over a wide range of entering group concentration. Good first-order rate plots were obtained covering three half-lives when the chloride concentration was 1.6 × 10^{-3} M (slightly less than the complex concentration). As the chloride concentration was reduced below 0.01 M, the first-order rate constants increased slightly. When the chloride concentration was maintained equal to the complex concentration and tetraphenylarsonium perchlorate added in amounts from 10^{-3} to 10^{-1} M the rate of chloride entry varied very much as it did in the presence of excess chloride. The rate of thiocyanate entry behaved differently. As the thiocyanate concentration was reduced below 0.01 M, the first-order rate constants decreased. At the lowest thiocyanate concentration, small deviation from a first-order rate plot was observed after one

half-life. The results of these studies are summarized in Fig. 1.

The kinetic results are sufficiently complicated to require some more definite information about the state of aggregation of electrolytes in this solvent. The complex ion *trans*-$[Co(en)_2NO_2NH_3]^{++}$ was chosen as a fairly faithful but unreactive model of *trans*-$[Co(en)_2$-$NO_2OH_2]^{++}$. The conductance of solutions of the perchlorate and chloride salts was determined in the concentration range 1×10^{-5} to 6×10^{-3} M. Plots of
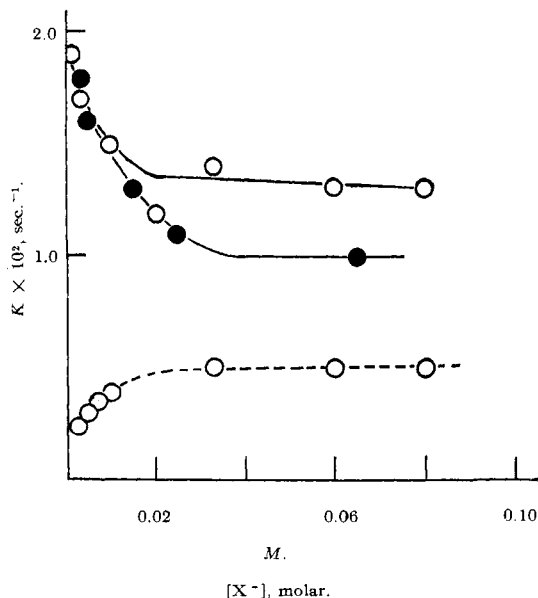

Fig. 1.—First-order anation rates of *trans*-$[Co(en)_2NO_2OH_2]^{++}$ as a function of anion concentration: O, X^- = chloride; ●, X^- = perchlorate. The entering anion is chloride at a concentration equal to the complex ion concentration: – – – –, X^- = thiocvanate. The complex concentration is 2×10^{-3} M for all points.

equivalent conductance (Λ) *vs.* (concentration)$^{1/2}$ are shown in Fig. 2. It is not possible to venture quantitative analysis of these data lacking information about limiting equivalent conductance at infinite dilution. Qualitatively, it is clear that association is important at the lowest concentrations and that the fraction of current-carrying species is rather small at the minimum concentrations useful for spectrophotometric kinetics. Outer sphere complexing to form *both* $[Co(en)_2NO_2NH_3]^{++}\cdots X^-$ and $X^-\cdots[Co(en)_2$-$NO_2NH_3]^{++}\cdots X^-$ is most probably important.

Discussion

The complicated kinetics in conjunction with conductivity data imply that the reactions observed are actually ligand interchanges between outer and inner coordination spheres. In this circumstance, we must look beyond the rate law for clues to the detailed mechanism. The broadest hint is contained in the result that the anation rate is not particularly sensitive to the nature of the entering anion. This seems to imply that the transition state of the reaction has, at most, a weak bond between cobalt and the entering anion. The contrary assumption requires that the transition state change substantially with the changing ability of the entering group to form a partial bond to cobalt, hence requires that the rate be sensitive to the nature of the anion.

Now, the assertion that all of the anation rates are very similar needs more careful examination. If the reactions take place in outer-sphere complexes, it is important to compare rates in similar aggregates. An attempt must be made to distinguish between anation in the 1:1 outer-sphere complex (ion pair) and anation in the 2:1 outer-sphere complex (ion triple) since the conductance results indicate the presence of both even at fairly low concentration. The results presented in Fig. 1 showing the concentration dependence of anation over a wide range of anion concentrations may be understood using reasonable assumptions about the degree of outer-sphere complexing. Looking at the conductance curves, we may conclude that 1:1 complexing is very nearly complete at all concentrations above 1×10^{-3} M in chloride since the equivalent conductance is leveling off at somewhat less than half of the maximum value even below this concentration. Further we see that perchlorate is less associated.
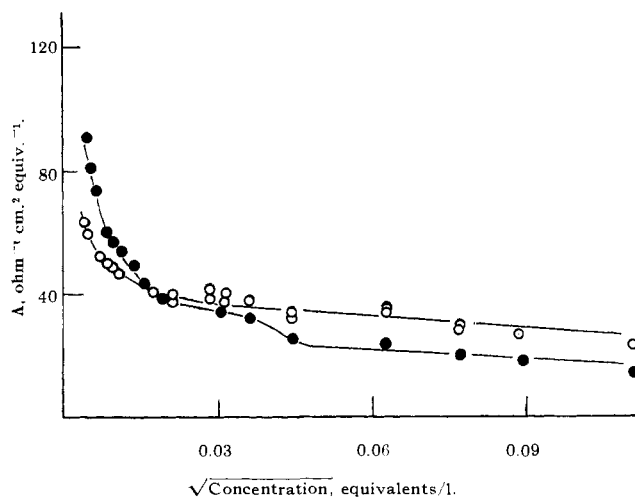

Fig. 2.—Equivalent conductance of salts of *trans*-$[Co(en)_2NO_2$-$NH_3]^{++}$ in 7.8% aqueous tetramethylene sulfone as a function of the square root of concentration: ●, the chloride salt; O, the perchlorate salt.

Extrapolating to the reaction system, the explanation for first-order kinetics of chloride entry even at low chloride concentrations is that the 1:1 complex is the predominant species at the lowest chloride concentrations. The effect of increasing chloride or adding perchlorate is to form the 2:1 outer-sphere complex which appears to react more slowly. The decrease in thiocyanate anation rates observed as the thiocyanate concentration is made small is explained by assuming that $[Co(en)_2NO_2OH_2]^{++}\cdots SCN^-$ dissociates, producing significant amounts of free $[Co(en)_2NO_2OH_2]^{++}$ at low total concentration. This idea is consistent with the observed departure from a first-order rate law. Langford's[7] observations that a wide variety of iodide and thiocyanate salts are more soluble in tetramethylene sulfone than their chloride or bromide analogs tend to support this interpretation. They probably indicate that thiocyanate is more effectively solvated than the halides. A few conductance data exist to suggest greater dissociation of iodides and thiocyanate in the sulfone.[7]

If these suggestions concerning degrees of association are correct, the rate of anation by thiocyanate at high thiocyanate concentration should probably be compared to the rate of anation by chloride extrapolated to zero

(7) C. H. Langford, Thesis. Northwestern University, Evanston, Ill., 1960.

chloride. These should be approximately the anation rates in 1:1 outer-sphere complexes and represent the extremes among this set of anions. The rate constants are 2×10^{-2} sec.$^{-1}$ for $[\mathrm{Co(en)_2NO_2OH_2}]^{++}\cdots\mathrm{Cl^-}$ and 5×10^{-3} for $[\mathrm{Co(en)_2NO_2OH_2}]^{++}\cdots\mathrm{SCN^-}$. Perhaps the factor of four separating the fastest anation rate from the slowest indicates that some degree of cobalt to anion bonding is important in the transition state, but we certainly cannot be confident that this is so. Different anions can produce sufficient differences in the electrostatic environment and in the organization of solvent molecules about the complex to account for much larger rate differences than those observed. Note that only SCN$^-$ is different.

The possibility that the complex is attacked by a sulfone molecule has been ignored above. This seems reasonable when excellent nucleophilic reagents (the anions) are present in the second coordination sphere. In addition, Langford and Tobe attempted to detect sulfone attack on a related complex under more favorable circumstances and rather definitely failed.[8]

The attacking groups used in this study were all mononegative ions. It is interesting to compare these results for outer sphere–inner sphere interchange with those quoted by Schmidt and Taube.[5] They give the first-order rate constants in aqueous solution for $[\mathrm{Co(NH_3)_5OH_2}]^{+3}\cdots\mathrm{OH_2}$, $[\mathrm{Co(NH_3)_5OH_2}]^{+3}\cdots\mathrm{SO_4^{-2}}$, and $[\mathrm{Co(NH_3)_5OH_2}]^{+3}\cdots\mathrm{H_2PO_4^-}$ as 3.5×10^{-4}, 1.1×10^{-4}, and 4.6×10^{-5} min.$^{-1}$, respectively. In their series, the entering groups differ in charge and hydrogen bonding properties and somewhat larger, yet still not large, rate differences are observed.

(8) C. H. Langford and M. L. Tobe, J. Chem. Soc., 506 (1963).